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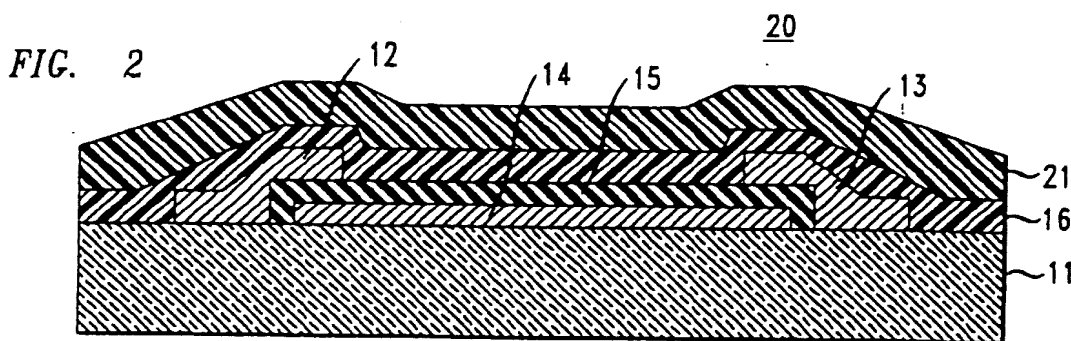
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### (54) Article comprising organic thin film transistors

(57) Articles according to an embodiment of the invention comprise an improved organic thin film transistor (TFT) that can have substantially higher source/drain current on/off ratio than conventional organic TFTs. An exemplary TFT (20) according to the invention comprises, in addition to a p-type first organic material layer (16) (e.g.,  $\alpha$ -6T), an n-type second organic material layer (21) (e.g., Alq) in contact with the first material layer. TFTs according to the invention can be advantageously

used in, for instance, active liquid crystal displays and electronic memories, and a preferred embodiment is expected to find wide use in complementary circuits. The preferred embodiments are organic TFTs that can be either n-channel or p-channel transistors, depending on biasing conditions. In a specific embodiment the transistor comprises a 15 nm thick layer of  $\alpha$ -6T (115) with a 40 nm thick layer of C<sub>60</sub> thereon (116). The latter was protected against degradation by the ambient by means of an appropriate electrically inert layer.



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for controlling, by means of a voltage applied to the third contact means, a current between the first and the second contact means. Significantly, the organic material comprises a layer of a first organic material of a first conductivity type and a layer of a second organic material of a second conductivity type that is in contact with the layer of the first organic material at least in a region between the first and second contact means and forms a p-n junction with the layer of first organic material, the layer of the first organic material being in contact with each of the first and second contact means and being not in contact with the third contact means. The third contact means generally can be identified with the gate contact in prior art devices, and the first and second contact means with the source and drain contacts of prior art devices.

Exemplarily, a TFT according to the invention has exhibited an on/off ratio of more than  $10^6$ , substantially higher than the ratios exhibited by prior art organic TFTs. The exemplary TFT according to the invention furthermore exhibited relatively high carrier mobility, in excess of  $0.003 \text{ cm}^2/\text{V}\cdot\text{s}$ . Desirably, TFTs according to the invention exhibit an on/off ratio greater than  $10^5$  at an operating gate voltage, and a carrier mobility of at least  $3 \times 10^{-3} \text{ cm}^2/\text{V}\cdot\text{s}$ , all at  $20^\circ\text{C}$ .

The layer of the first organic material in TFTs according to the invention can comprise any of the organic materials known to be suitable for use as the active layer in organic TFTs. Among these materials are polythiophene and substituted derivatives thereof such as poly(3-hexylthiophene and poly(3-octylthiophene) polythienylenevinylene,  $\alpha$ -hexathienylene ( $\alpha$ -6T) and substituted derivatives thereof such as  $\alpha$ ,  $\omega$ -dihexyl- $\alpha$ -6T. Other suitable first organic materials are disclosed in US patent 5,315,129 and in G. Horowitz et al., Synthetic Metals, Vol. 41-43, pp. 1127-1130. Exemplarily, the first organic material is selected from polymers of thiophene of degree of polymerization greater than three (and typically less than 9), polymers of substituted derivatives of thiophene, and poly(thienylenevinylene). Recently we have shown that 2, 2'-bis (benzo [1,2-b: 4,5-b']dithiophene can have p-type mobility of  $\approx 10^{-4} \text{ cm}^2/\text{V}\cdot\text{s}$  in a TFT, with excellent on/off ratio and thermal stability. This compound, as well as its tris analog and substituted derivatives, is contemplated for use in TFTs according to the invention.

The above recited compounds are p-type organic semiconductors, but the invention is not so limited. We currently believe that other organic compounds that can be deposited in thin film form and that are n-type are also likely to be suitable for use as the first organic material in transistors according to the invention, and use of these compounds is contemplated. We currently prefer first organic semiconductor materials that can be deposited in crystalline (typically polycrystalline) form, but amorphous layers may also have utility.

Among the second organic materials that are suitable for use in the invention is  $\text{C}_{60}$ . However, the inven-

tion is not so limited, and the use of other organic materials, including p-type materials, is contemplated. Among n-type organic semiconductors that are likely to be useful are other fullerenes (e.g.,  $\text{C}_{70}$  and homologs), perylene tetracarboxylic anhydrides and imides and substituted derivatives (e.g., perylene tetracarboxylic dianhydride or PTCDA), oxadiazole compounds, tetracyanoquinodimethanes (e.g., 7, 7, 8, 8-tetracyanoquinodimethane and its dibenzo derivative), porphyrins and quinones. Exemplary substituents are nitro, cyano, halo and perfluoroalkyl substituents, with other alkyls also being potentially useful. Those skilled in the art will appreciate that not all n-type organic semiconductor materials will necessarily be useful in the practice of this invention. Indeed, there are materials (e.g., Alq) that are useful in some embodiments of the invention but are currently not thought to be useful in other embodiments.

In a first exemplary embodiment of the invention the transistor further comprises a dielectric layer disposed between the third contact means and both of the first and second contact means, with the first organic material layer in contact with the dielectric layer. Transistors of this embodiment have a structure analogous to that of conventional metal-insulator-semiconductor (MIS) FETs and will be referred to as organic TFTs of the MIS-FET type.

In a second exemplary embodiment the third contact means of the transistor are disposed on the second organic material layer and are spaced from the first organic material layer. Transistors of this embodiment have a structure analogous to that of conventional junction FETs (J-FETs) and will be referred to as organic TFTs of the J-FET type.

A third exemplary embodiment is similar to the above first embodiment, but with the order of the first and second organic material layers interchanged.

Transistors according to the invention are advantageously used in articles such as display systems, memories, and other analog and/or digital circuits.

A further embodiment of the invention is an organic thin film transistor capable of operation as either a p-channel or n-channel device, and multi-transistor circuits that comprise such transistors. These TFTs do not necessarily possess as high on/off ratios as do some of the previously disclosed p-channel TFTs.

#### Brief Description of the Drawings

FIG. 1 schematically shows an exemplary prior art organic TFT;

FIGs. 2-4 schematically show exemplary transistors according to the invention;

FIGs. 5 and 6 show performance data of a MIS-FET-type transistor before and after provision of a second organic material layer;

FIG. 7 shows performance data of a J-FET-type transistor according to the invention;

FIGs. 8 and 9 schematically show the band edge

## Description

### Field of the Invention

This invention pertains to thin film transistors (TFTs), more specifically, to TFTs that comprise organic active layer material.

### Background of the Invention

Thin film transistors (TFTs) are known, and are of considerable commercial significance. For instance, amorphous silicon-based TFTs are used in a large fraction of active matrix liquid crystal displays.

TFTs with an organic active layer are also known. See, for instance, F. Garnier et al., *Science*, Vol. 265, pp. 1684-1686; H. Koezuka et al., *Applied Physics Letters*, Vol. 62 (15), pp. 1794-1796; H. Fuchigami et al., *Applied Physics Letters*, Vol. 63 (10), pp. 1372-1374; G. Horowitz et al., *J. Applied Physics*, Vol. 70 (1), pp. T469-475, and G. Horowitz et al., *Synthetic Metals*, Vol. 41-43, pp. 1127-1130. These devices typically are field effect transistors (FETs). Such devices potentially have significant advantages over conventional TFTs, including a potentially simpler (and consequently cheaper) fabrication process, the possibility for low temperature processing, and compatibility with non-glass (e.g., plastic) substrates. Bipolar transistors that utilize both p-type and n-type organic material are also known. See, for instance, US patent 5,315,129. S. Miyauchi et al., *Synthetic Metals*, 41-43 (1991), pp. 1155-1158, disclose a junction FET that comprises a layer of p-type polythiophene on n-type silicon.

However, despite considerable research and development effort, "organic" TFTs have not yet reached commercialization, at least in part due to relatively poor device characteristics of prior art organic TFTs.

An important device characteristic of a switching transistor is the on/off ratio of the source/drain current. Prior art organic TFTs typically have relatively low on/off ratios. For instance, H. Fuchigami et al. (op. cit.) recently reported a device that had carrier mobility comparable to amorphous silicon, but had an on/off ratio of only about 20 at -30V gate-source voltage. That paper also discloses purification of semiconducting materials to reduce the carrier scattering by impurities.

H. Koezuka et al. (op. cit) report attainment of an on/off ratio (modulation ratio) of the channel current of about  $10^5$  in a device with doped polypyrrole-coated (a highly conducting polymer) source and drain contacts. According to these authors, this is the highest on/off ratio achieved in organic FETs. Nevertheless, the reported on/off ratio is still substantially smaller than on/off ratios typically available in conventional FETs and demanded for many potential applications of organic TFTs. Furthermore, the organic TFT had very low carrier mobility ( $2 \times 10^{-4} \text{ cm}^2/\text{V}\cdot\text{s}$ ), and thus would not have been suitable for high-speed operation. European patent application

No. 92307470.2 (publication No. 0 528 662 A1) discloses an organic FET that comprises a first organic layer that constitutes a channel between source and drain electrodes and is in contact with a second organic layer that is disposed between the gate electrode and the source and drain electrodes. The first and second organic layers are of the same conductivity type but differ in their carrier concentration.

In view of the potential significance of organic TFTs, it would be desirable to have available such devices that have improved characteristics, including improved on/off ratio of the source/drain current. This application discloses such devices, and a method of making the devices.

US patent application Serial No. 08/404,221, filed March 15, 1995 by R. C. Haddon et al., discloses a  $\text{C}_{60}$ -based organic transistor. See also A. Dodabalapur et al., *Science*, Vol. 268, p. 270 (1995).

### Definitions and Glossary

An "organic semiconductor" herein is a material that contains a substantial amount of carbon in combination with other elements, or that comprises an allotrope of elemental carbon (excluding diamond), and exhibits charge carrier mobility of at least  $10^{-3} \text{ cm}^2/\text{V}\cdot\text{s}$  at room temperature ( $20^\circ\text{C}$ ). Organic semiconductors of interest herein will typically have conductivity less than about  $1 \text{ S/cm}$  at  $20^\circ\text{C}$ .

A "p-type" ("n-type") organic semiconductor herein is an organic semiconductor in which the Fermi energy is closer to (farther from) the energy of the highest occupied molecular orbital (HOMO) of the molecules or aggregates present in the material than it is to (from) the energy of the lowest unoccupied molecular orbital (LUMO). The term is also intended to mean an organic semiconductor which transports positive charge carriers more (less) efficiently than negative carriers. Positive (negative) carriers are generally referred to as "holes" ("electrons").

An organic "p-n junction" herein is the contact region between a p-type and a n-type organic semiconductor.

### Summary of the Invention

In a broad aspect the invention is embodied in an article that comprises a novel organic TFT that can have substantially improved characteristics (e.g., on/off ratio), as compared to prior art organic TFTs. Some embodiments of the invention can exhibit p-channel or n-channel transistor behavior, depending on biasing conditions, and need not necessarily have high on/off ratio.

Specifically, the organic TFT comprises organic material, spaced apart first and second contact means (e.g., gold electrodes) in contact with the organic material, and third contact means that are spaced from each of the first and second contact means and that are adapted

tric. It will be understood that in this embodiment layer 42 is n-type organic semiconductor material.

The data of FIG. 7 were obtained from a TFT of the general type shown in FIG. 3. Specifically, the substrate was SiO<sub>2</sub>-coated Si. An inter-digitated set of source/drain electrodes (10 nm Cr/30 nm Au) were formed on the substrate. The width and spacing of the fingers of the digitated structure was 10 $\mu$ m; the overall dimensions of the structure are 2 mm x 2 mm. A 50 nm layer of  $\alpha$ -6T was evaporated over the interdigitated structure, and a 60 nm layer of Alq was evaporated onto the  $\alpha$ -6T layer. A 100 nm thick and 3 mm wide finger of Al, defined by means of a shadow mask, was deposited on the Alq layer so as to extend across the source/drain spacing. The Al finger served as the gate electrode.

Transistors according to the invention can be produced by any appropriate method on any suitable substrate. Exemplary substrates are glass, plastics such as MYLAR® or KAPTON®, or Si (coated with SiO<sub>2</sub> or uncoated).

Although provision of a second organic material layer will generally result in improved device characteristics if the first organic material is of a purity that is conventionally found in prior art devices, we have also found that, at least in the case of devices that comprise  $\alpha$ -6T, the use of higher purity first organic material may result in additional improvement in device characteristics. Techniques for purifying  $\alpha$ -6T are described in co-assigned US patent application entitled "Method of Making an Organic Thin Film Transistor, and Article Made by the Method", Serial No. 08/353,032, filed December 9, 1994.

We have also found that an appropriate heat treatment of the deposited first organic material (e.g.,  $\alpha$ -6T) can change the morphology of the layer, and consequently further improve device characteristics. More specifically, we have found that rapid thermal annealing (RTA) of deposited films of  $\alpha$ -6T can substantially increase the grain size of the material, to the extent that average grain size can exceed the channel length (typically 4 - 12 $\mu$ m) of the intended TFT. If this is the case then the active material can behave substantially like a single crystal.

Typical as-deposited films of  $\alpha$ -6T are polycrystalline, with average grain size of about 100 nm or less. Annealing such films for a short time (typically less than 10 seconds, e.g., 1 second) at a temperature close to, the melting point (e.g., 295-315°C) exemplarily has resulted in increase of the average grain size to above 2 $\mu$ m, exemplarily about 5 - 100 $\mu$ m. Annealing is desirably in an inert atmosphere, e.g. N<sub>2</sub>. Any suitable heat source (e.g., a bank of halogen lamps focused to a susceptor, or a graphite strip heater) can be used.

Although in many cases the carrier mobility in the p-type material will be substantially higher than the mobility in the n-type material (exemplarily by a factor of 100 or more), it may at times be advantageous if the respective mobilities in the two materials are compara-

ble (e.g., are within a factor of about 10 of each other). If this is the case then it will be possible, by appropriate biasing of the gate electrode in a MIS-FET type structure such as is shown in FIG. 2, to obtain either an n-channel or a p-channel transistor. Those skilled in the art will recognize that the ability to form either n- or p-channel transistors makes possible fabrication of complementary circuits, and we contemplate use of TFTs according to the invention as building blocks in complementary analog and/or digital circuits. Such TFTs need not possess very high on/off ratio in order to be useful.

Transistors according to one embodiment of the invention can be used as discrete devices but will more typically be used in integrated circuits that comprise a multiplicity of transistors according to the invention, possibly in conjunction with conventional semiconductor devices, with conductors interconnecting the devices and providing means for energizing the devices, providing input signals to the circuit and optionally receiving output signals therefrom.

By way of example, transistors according to the invention are used as current switches in liquid crystal displays in functionally the same way as prior art semiconductor TFTs are currently used. This is schematically illustrated in FIG. 10, which is based on an illustration at p. 102 of "Amorphous and Microcrystalline Devices", J. Kanicki, editor, Artech House, Boston (1991). FIG. 10 depicts relevant aspects of an exemplary circuit diagram of an active-matrix liquid crystal display, wherein transistors 101 are TFTs according to the invention, and the remainder of the circuit is conventional. Numerals 102 refer to liquid crystal, and numerals 103-105 refer to signal lines, gate lines and common electrode, respectively. Video signals and gate pulses are also shown schematically.

FIG. 11 schematically depicts an exemplary organic thin film transistor according to the invention. The transistor is capable of p-channel and n-channel operation in a single device. Reference numerals 110-116 refer to the silicon substrate which serves as the gate, the gate dielectric (SiO<sub>2</sub>), the gate contact (Au), the source (Au), the drain (Au), the p-type organic layer ( $\alpha$ -6T) and the n-type organic layer (C<sub>60</sub>), respectively. As those skilled in the art will recognize, the transistor of FIG. 11 closely resembles that of FIG. 2. As those skilled in the art will recognize, either or both of layers 115 and 116 can comprise more than one organic compound.

In a currently preferred embodiment the p-type layer consists of  $\alpha$ -6T, is typically about 10-20 nm thick, and is disposed on the gate dielectric. The n-type layer consists of C<sub>60</sub>, is typically about 20-40 nm thick, and is disposed on the p-type layer. It is typically desirable to provide an electrically inactive layer (e.g., SiO) on the n-type layer, to protect the n-type layer from the ambient.

It is not a requirement that the p-type material is disposed below the n-type material. However, we have attained better device characteristics for such transistors,

alignment of isolated  $\alpha$ -6T and Alq, and the band edges of  $\alpha$ -6T in contact with Alq;

FIG. 10 shows an exemplary drive circuit in an active matrix liquid crystal display that comprises TFTs according to the invention;

FIG. 11 schematically depicts an exemplary organic thin film transistor capable of p-channel and n-channel operation in a single device;

FIG. 12 shows the relevant energy levels of Au,  $\alpha$ -6T and C<sub>60</sub>; FIGs. 13 and 14 show energy band diagrams of the transistor according to the invention in the p-channel and n-channel enhancement mode, respectively;

FIGs. 15 and 16 show transistor characteristics for p-channel and n-channel operation, respectively;

FIG. 17 shows further transistor characteristics; and FIG. 18 schematically shows an exemplary circuit comprising n- and p-channel transistors according to the invention.

### Detailed Description

Prior art organic TFTs typically are MIS-FET-type or hybrid J-FET-type transistors and can be embodied in a variety of structures. An exemplary prior art MIS-FET-type TFT (10) with organic active layer is schematically depicted in FIG. 1, wherein numerals 11-16 refer, respectively, to the substrate (e.g., glass, plastic, metal, semiconductor), source electrode, drain electrode, gate electrode, gate insulator layer and organic active material (organic semiconductor) layer. As those skilled in the art will appreciate, means for causing the flow of charge carriers between source and drain, and means for applying a voltage to the gate electrode will be present in a working device but are not shown.

FIG. 2 schematically shows an exemplary MIS-FET-type device (20) according to the invention. Numerals 11-16 refer to elements that respectively correspond to elements of the same reference numeral in FIG. 1, and numeral 21 refers to an organic material layer that is of the opposite conductivity type as layer 16, and forms a p-n junction therewith. Exemplarily, layer 16 is p-type (e.g.,  $\alpha$ -6T) and layer 21 is n-type (e.g., Alq).

We have discovered that provision of an appropriate layer 21 can result in substantially improved device performance, typically a significant decrease in the "off" current between source and drain, with corresponding increase in the on/off ratio of the transistor.

We currently believe that the decrease in the "off" current is associated with the contact between appropriate organic layers 16 and 21, e.g., the  $\alpha$ -6T/Alq interface, and attendant depletion of the (p-type) residual carriers in the layer (e.g., 16) of first organic material.

By analogy with conventional p-n junctions, it can be said that the width W of the depletion layer formed at the first/second organic material interface at zero bias is  $(2\epsilon_1 V_b / q N_1)^{1/2}$ , where  $\epsilon_1$  is the dielectric constant of the first organic material,  $V_b$  is the "built-in" potential

$E_{F1} - E_{F2} / q$ .  $N_1$  is the free carrier density in the first organic material, q is the elementary charge ( $1.6 \times 10^{-19}$  C), and  $E_{F1}$  and  $E_{F2}$  are the Fermi energy in the first and second organic materials, respectively. In the above expression for W it is assumed that the second organic material has much higher free carrier density than the first organic material.

We currently believe that the presence of a depletion region of non-zero width at zero bias results in lower current between the first and second contact means ( $I_D$ ) at zero bias by causing many of the free carriers in the first organic material layer to be electrically inactive.

The above remarks are offered for tutorial reasons only, and are not intended to limit the claims.

A significant feature of transistors according to the invention is a relatively large (e.g.,  $\geq 0.5V$ ) value of  $V_{bi}$ . This in turn requires a relatively large difference in Fermi energy between the first and second organic materials.

This is exemplarily illustrated in FIGs. 8 and 9, which schematically respectively show the band edge alignment of isolated  $\alpha$ -6T and Alq, and the band edges of  $\alpha$ -6T in contact with Alq. As is well known,  $\alpha$ -6T and Alq are recognized as p-type and n-type organic semiconductors, respectively. The numerical values in FIG. 8 are in electron volts, and numerals 91-93 in FIG. 9 refer to insulator,  $\alpha$ -6T and Alq, respectively.

FIGs. 5 and 6 show comparative data for a MIS-FET-type organic TFT without and with second organic material layer, respectively. The data of FIG. 5 were obtained from a transistor of the type shown in FIG. 2, but without layer 21. The substrate was silicon, the gate contact was a 30 nm thick gold stripe. The gate dielectric was a 300 nm thick layer of conventionally formed SiO<sub>2</sub>. The gold source and drain electrodes were 30 nm thick, 250  $\mu$ m long and 100  $\mu$ m wide, and were spaced apart by a distance of 12  $\mu$ m. The p-type organic semiconductor layer was 50 nm thick  $\alpha$ -6T. The data of FIG. 6 were obtained from the above described transistor, but with a 60 nm thick Alq layer deposited on the  $\alpha$ -6T layer. As can be seen from the figures, provision of the Alq layer resulted in a significant decrease in drain current ( $I_D$ ) at zero gate bias ( $V_G = 0$ ), exemplarily from -1.1  $\mu$ A to -68 nA.

FIG. 7 shows similar performance data for a J-FET-type organic TFT according to the invention. As can be seen, the device has desirably low  $I_D$  at  $V_G = 0$ . FIG. 3 schematically depicts a J-FET-type organic TFT (30) according to the invention, with numerals 31-36 designating the insulating substrate, first organic material layer, second organic material layer, first contact means, second contact means, and third contact means, respectively.

FIG. 4 schematically depicts a further exemplary embodiment of the invention that corresponds to the above described third embodiment. Numerals 41-47 refer, respectively, to the substrate, first organic semiconductor layer, second organic semiconductor layer, first contact, second contact, third contact, and gate dielec-

FIGs. 15-17 show characteristics of a particular one of the thus produced TFTs.

# Claims

1. An article comprising a thin film transistor (e.g., 20) comprising

- a) a quantity of organic material;
- b) spaced apart first and second contact means (12, 13) in contact with said quantity of organic material; and
- c) third contact means (14) that are spaced from each of said first and second contact means and that are adapted for controlling, by means of a voltage applied to the third contact means, a current between the first and the second contact means;

## CHARACTERIZED IN THAT

- d) the quantity of organic material comprises a layer (16) that comprises a first organic material of a first conductivity type and a layer (21) that comprises a second organic material of a second conductivity type, said second organic material being in contact with said first organic material at least in a region between said first and second contact means.

2. Article according to claim 1, wherein the first organic material is a p-type organic material and the second organic material is an n-type organic material.
3. Article according to any of claims 1 and 2, wherein the article comprises a plurality of said transistors, with at least a first of said transistors biased to form an n-channel transistor, and at least a second of said transistors biased to form a p-channel transistor, said first and second transistors being otherwise essentially identical.
4. Article according to claim 3, wherein the p-type and n-type organic materials are selected such that the LUMO and HOMO of the p-type organic material is closer to a vacuum energy level than the HOMO of the n-type organic material, where "LUMO" and "HOMO" mean "lowest unoccupied molecular orbital" and "highest occupied molecular orbital", respectively.
5. Article according to claim 4, wherein the p-type organic material is selected from the group consisting of polymers of thiophene of degree of polymerization greater than 3 and less than 9, polymers of substituted derivatives of thiophene, poly (thienylenevinylene), and 2, 2'-bis (benzo [1, 2-b: 4, 5-b'] dithiophene.

6. Article according to claim 5, wherein the n-type organic material is selected from the group consisting of the fullerenes, perylene tetracarboxylic anhydrides and imides and their substituted derivatives, oxadiazole compounds, tetracyanoquinodimethanes and dibenzo derivatives thereof, porphyrins and quinones.

7. Article according to claim 6, wherein the p-type organic material is  $\alpha$ -6T and the n-type organic material is  $C_{60}$ .

8. Article according to claim 3, wherein the p-type organic material is in contact with said first and second contacts.

9. Article according to claim 1, further comprising a quantity of material or combination of materials disposed on one of said layers of organic material and selected to essentially prevent contact of an ambient atmosphere with said layers of organic material.

as compared to transistors having the p-type layer disposed on the n-type layer. Furthermore, we have observed degradation of n-channel operation if the p-type layer is relatively thick (typically  $\geq 40\text{nm}$ ). It thus appears desirable that the p-type layer is relatively thin ( $<40\text{ nm}$ , preferably  $<20\text{ nm}$ ).

The energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbitals (LUMO)  $\alpha$ -6T and  $C_{60}$  are shown in FIG. 12. As those skilled in the art will recognize, these energy levels are such that, when the gate is biased negatively with respect to the source, the p-channel material ( $\alpha$ -6T) is filled with holes, and when the gate is biased positively with respect to the source, the n-channel material ( $C_{60}$ ) is filled with electrons.

FIGs. 13 and 14 schematically show the energy band diagrams of an exemplary transistor according to FIG. 11 in the p-channel and n-channel modes of operation, respectively. In the p-channel mode an accumulation layer of holes is formed in the  $\alpha$ -6T near the  $\alpha$ -6T/ $\text{SiO}_2$  interface, and in the n-channel mode an accumulation layer of electrons is formed in  $C_{60}$  near the interface with  $\alpha$ -6T. FIGs. 13 and 14 assume an applied bias of  $-30\text{ V}$  and  $+60\text{ V}$ , respectively. Numerals 130 and 140 refer to the Fermi levels, and numeral 131 refers to the energy level of the metal contact.

FIGs. 15 and 16 show drain current vs. drain voltage for an exemplary transistor according to FIG. 11, for p-channel and n-channel operation, respectively. It is to be emphasized that the data of FIGs. 15 and 16 were obtained from a single transistor, establishing that one and the same transistor can serve as either a p-channel or n-channel device. The dotted lines in FIG. 16 represent drain currents at low positive gate fields.

Although the discussion of complementary organic thin film transistors was in terms of  $\alpha$ -6T/ $C_{60}$ -based transistors, the invention is not so limited. We have, for instance, achieved results qualitatively similar to those of FIGs. 15 and 16 with a transistor of the type shown in FIG. 11, but with  $\alpha$ ,  $\omega$  hexyl 6T substituted for  $\alpha$ -6T, and we expect that many of the above recited first organic materials are suitable for use in p- and n-channel organic thin film transistors, provided they are used in a combination that has an energy band line-up similar to that of the  $\alpha$ -6T/ $C_{60}$  combination of FIG. 12, and has appropriate transport properties. Specifically, the LUMO and HOMO of the p-channel materials must be closer to the vacuum level than the HOMO of the n-channel material.

The data of FIGs. 15 and 16 were analyzed with a model that takes into account short-channel effects, parasitic resistance, and field dependence of the carrier mobility. The p-channel mobility is about  $4 \times 10^{-3} \text{ cm}^2/\text{V}\cdot\text{s}$ , and the threshold voltage is about  $0\text{ V}$ . The n-channel mobility is about  $5 \times 10^{-3} \text{ cm}^2/\text{V}\cdot\text{s}$ , and the n-channel threshold voltage is about  $+40\text{V}$ . The asymmetry of device characteristics may be related to the fact that the HOMO energy of  $\alpha$ -6T almost exactly matches the work function of Au, but that the LUMO energy of

$C_{60}$  matches the Au work function only relatively poorly, with a potential barrier of  $>1\text{V}$  existing between the work function and the LUMO level. It is however expected that optimization of the contact metallization and device geometry will reduce both the n-channel threshold voltage and the n-channel source-drain offset voltage.

Complementary circuits that utilize conventional (i. e., Si-based) transistors are well known, and are known to be capable of operation with low power dissipation, see, for instance, W. N. Carr et al., "MOS/LSI Design and Applications", McGraw-Hill, especially pp. 77-78. In conventional complementary circuits it is predetermined (through choice of dopant) which transistor will be n-channel and which will be p-channel.

Transistors according to one embodiment of the invention can be either p-channel or n-channel, depending on the applied bias, and thus can provide the circuit designer an additional degree of freedom, since a given transistor can be a p-channel device under one set of bias conditions, and a n-channel device under another set of bias conditions.

FIG. 18 schematically shows an exemplary complementary circuit, an inverter, that comprises two substantially identical transistors according to the invention, with one of the transistors operating as an n-channel device and the other operating as a p-channel device.

Example: A thermally oxidized n-type Si wafer ( $\text{SiO}_2$  thickness  $\sim 0.3\mu\text{m}$ ) was carefully cleaned in acetone and methanol, followed by a rinse in DI water. The  $\text{SiO}_2$  was removed from predetermined portions of the wafer in conventional manner by etching in buffered oxide etch (BOE) solution. Gold contact pads were deposited on predetermined portions of both the exposed Si and the  $\text{SiO}_2$  in conventional fashion, with the pads on the Si to function as gate contact, and the pads on the  $\text{SiO}_2$  to function as source and drain contacts, all in a TFT substantially as shown in FIG. 11. Gate lengths were between  $1.5$  and  $25\mu\text{m}$ , and the pad width was  $250\mu\text{m}$ . The thus prepared wafer was loaded into a thermal evaporator (base pressure  $< 10^{-6}$  Torr). A quantity of  $\alpha$ -6T, prepared and purified substantially as disclosed in US patent application Serial No. 08/353,032, was present in the evaporator, as was a quantity of  $C_{60}$ , prepared substantially as disclosed in R. C. Haddon et al., ACS Symposium Series No. 481 (1992), p. 71, and in the above cited '221 US patent application. A  $15\text{ nm}$  film of  $\alpha$ -6T was first sublimed over the substrate, followed by sublimation of a  $40\text{ nm}$  film of  $C_{60}$ , both at rates in the range  $0.5 - 10\text{ nm/s}$ . Deposition of the  $C_{60}$  film was followed by sublimation of a  $45\text{ nm}$  film of  $\alpha$ -6T to protect the  $C_{60}$  from the ambient. We have found that exposure to oxygen leads to degradation of transport properties in  $C_{60}$ , and may lead to such degradation also in other n-type semiconductors.

Subsequent to the deposition of the protective (electrically inactive)  $\alpha$ -6T film, the wafer was removed from the evaporation chamber and quickly loaded into a vacuum probe station for transistor characterization.

FIG. 5

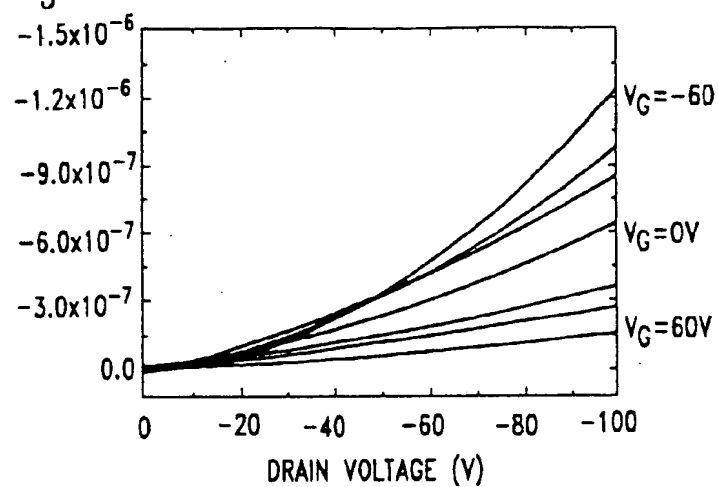


FIG. 6

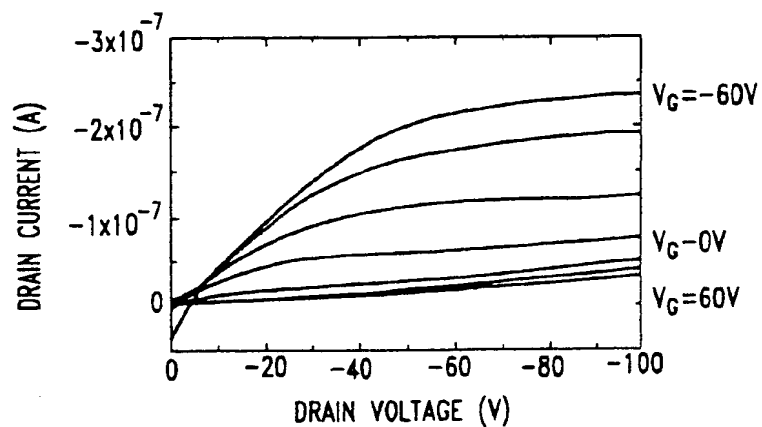


FIG. 7

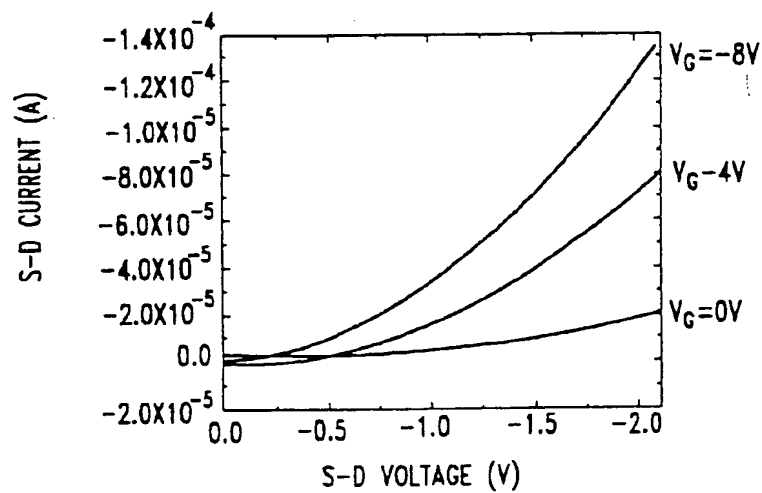




FIG. 1  
(PRIOR ART)

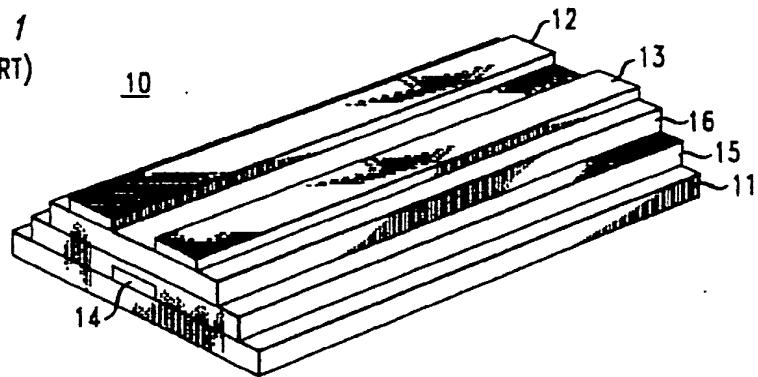


FIG. 2

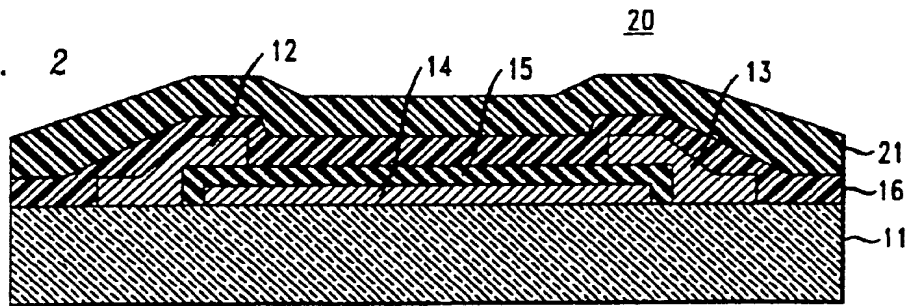


FIG. 3

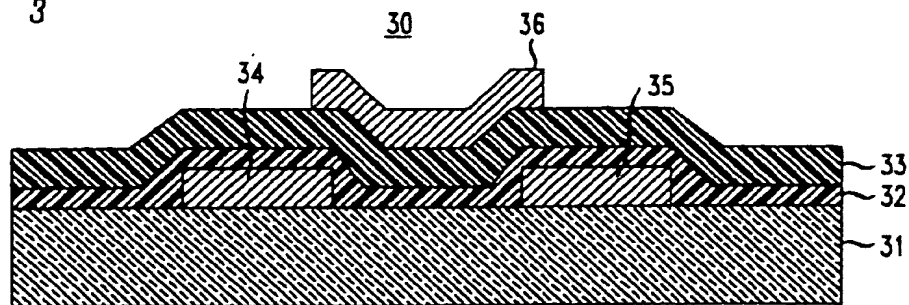
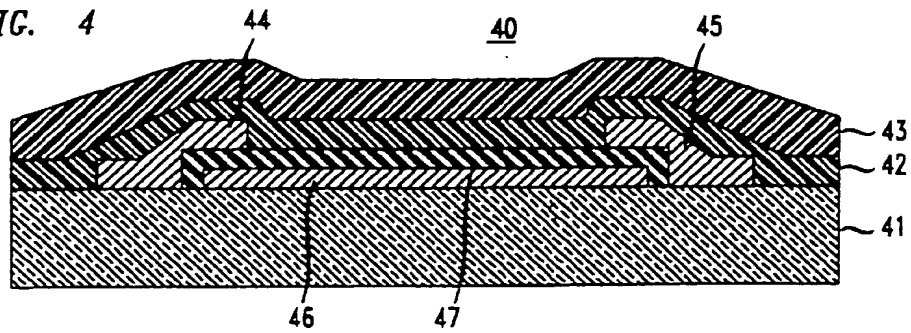
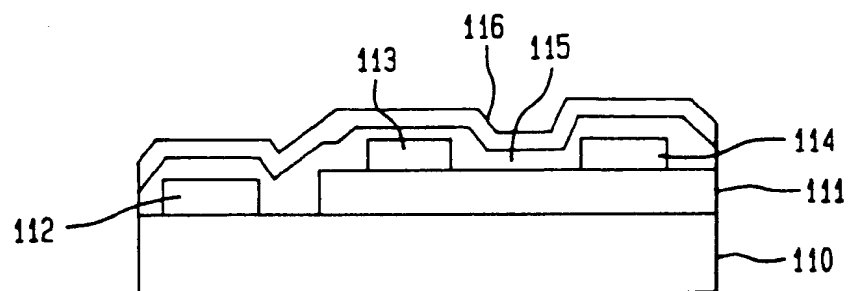


FIG. 4



**FIG. 11**



**FIG. 12**

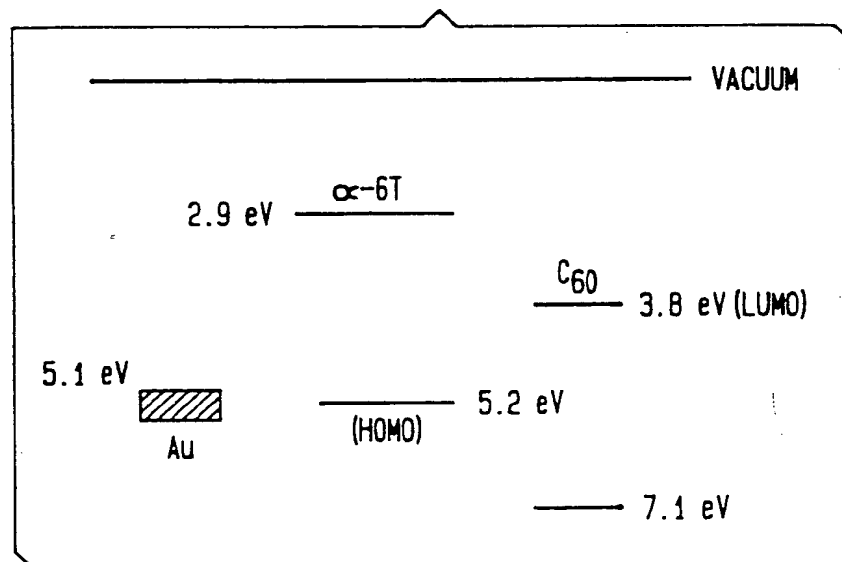


FIG. 8

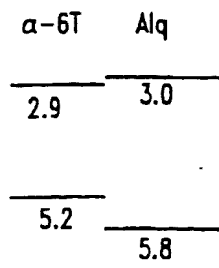


FIG. 9

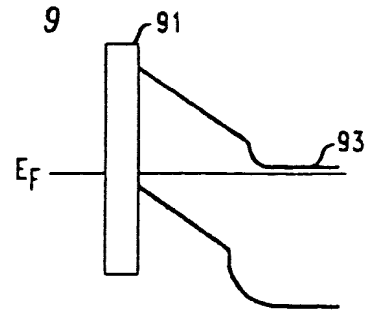


FIG. 10

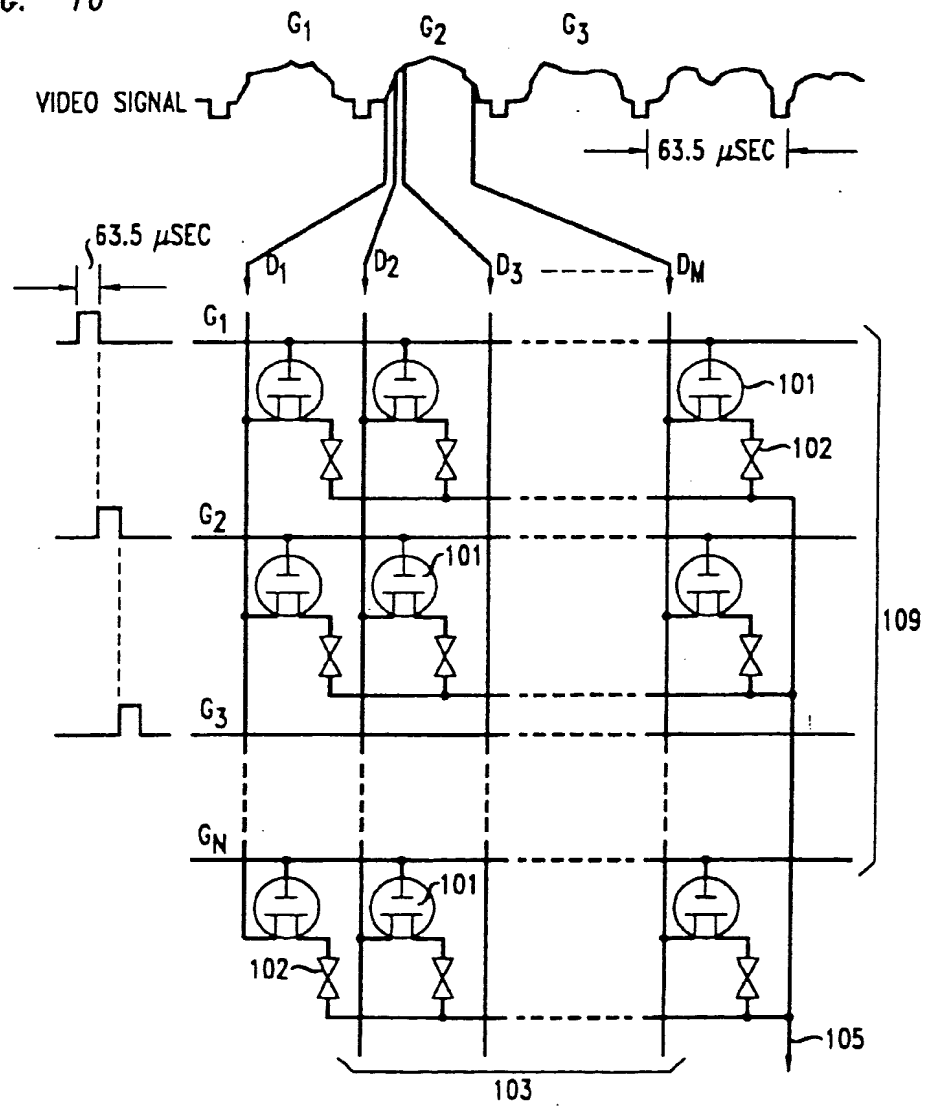


FIG. 15

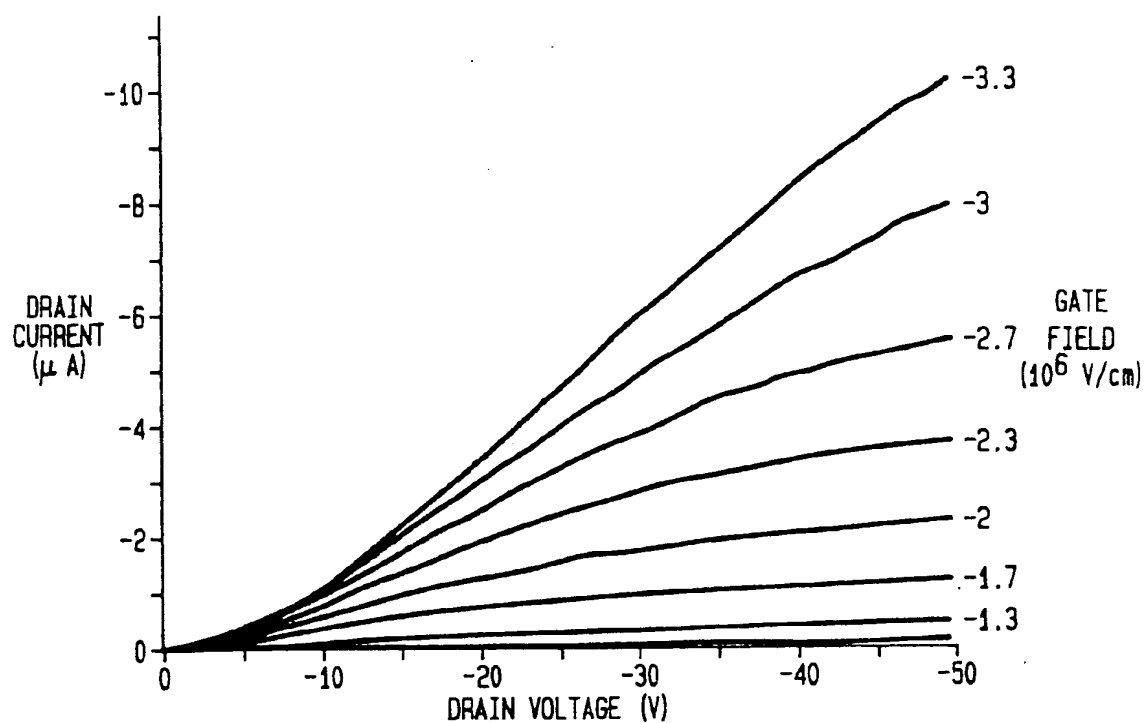


FIG. 16

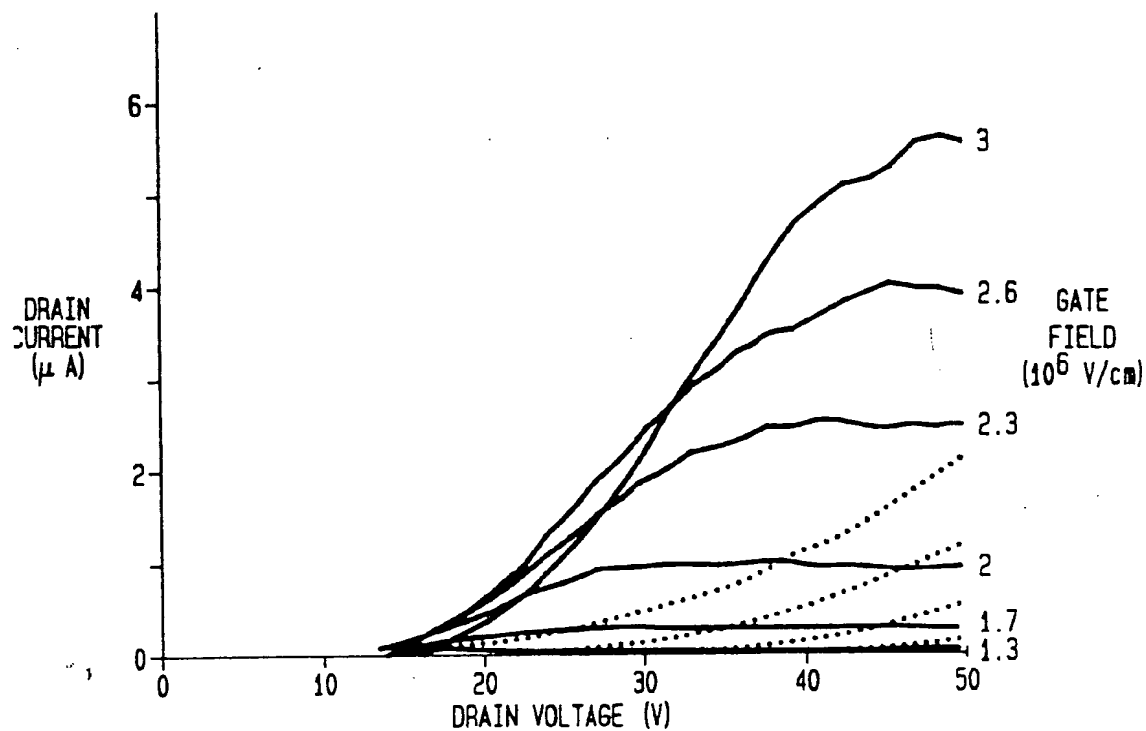


FIG. 13

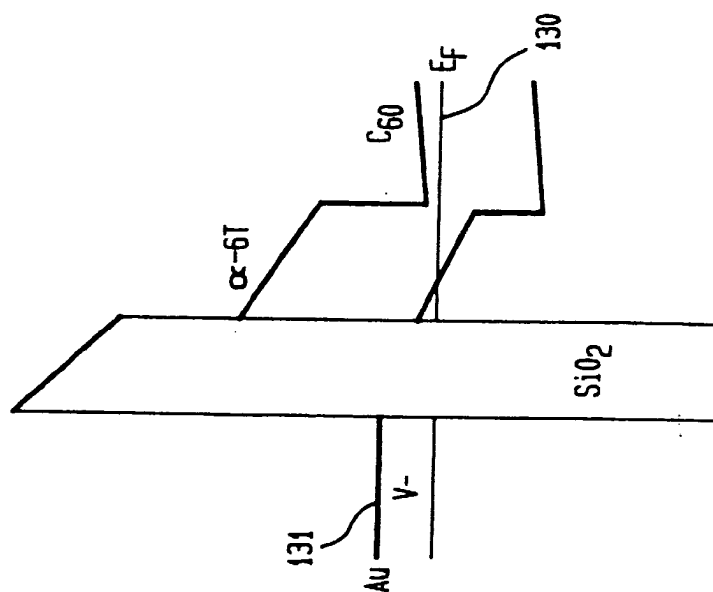
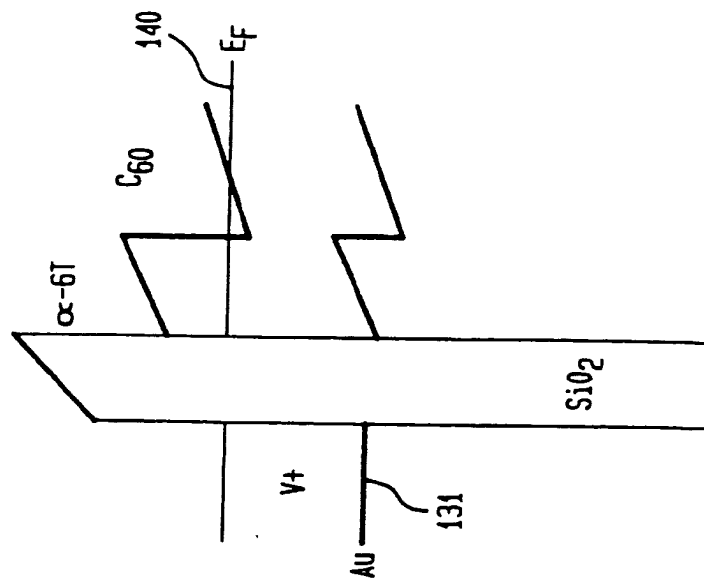


FIG. 14



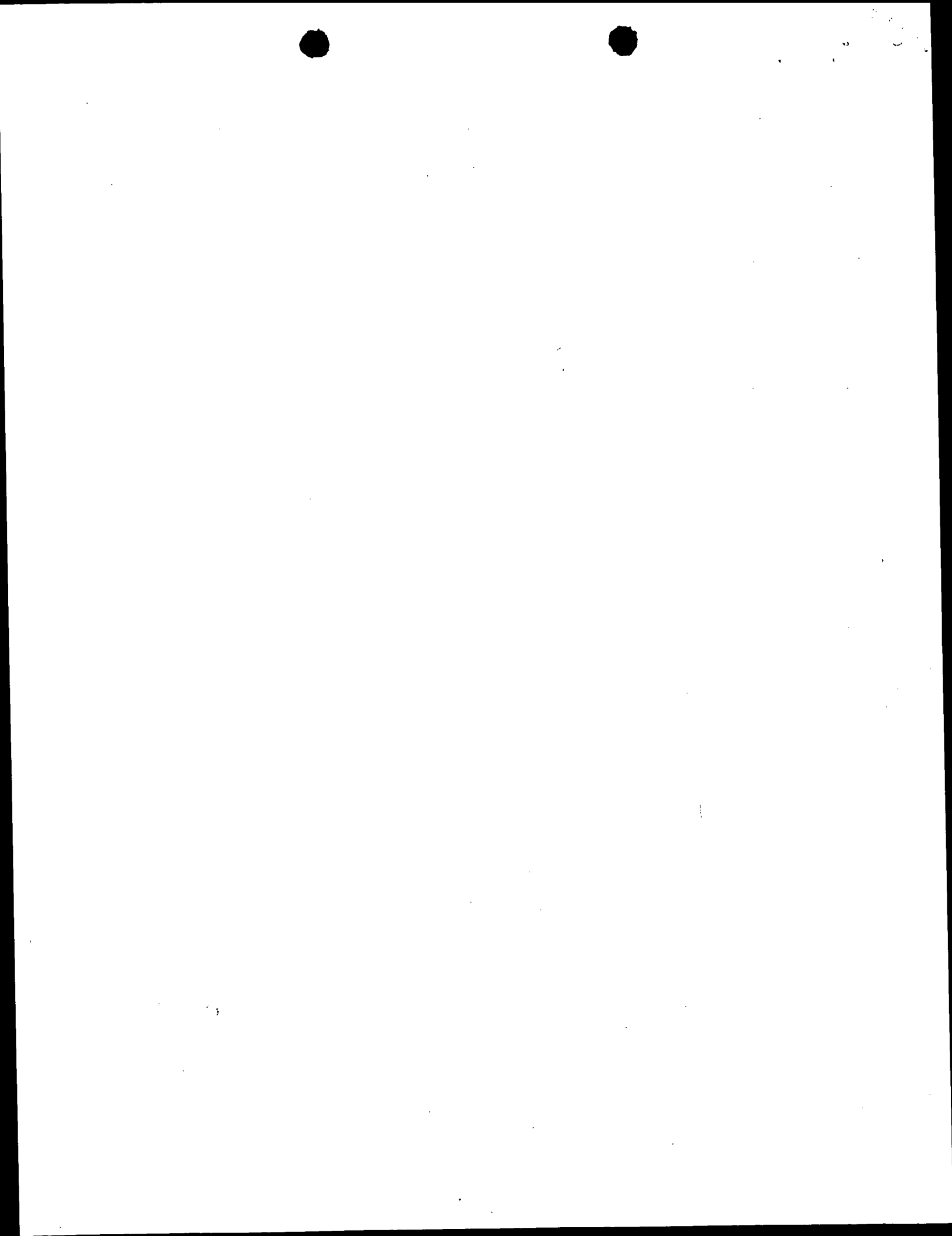


FIG. 17

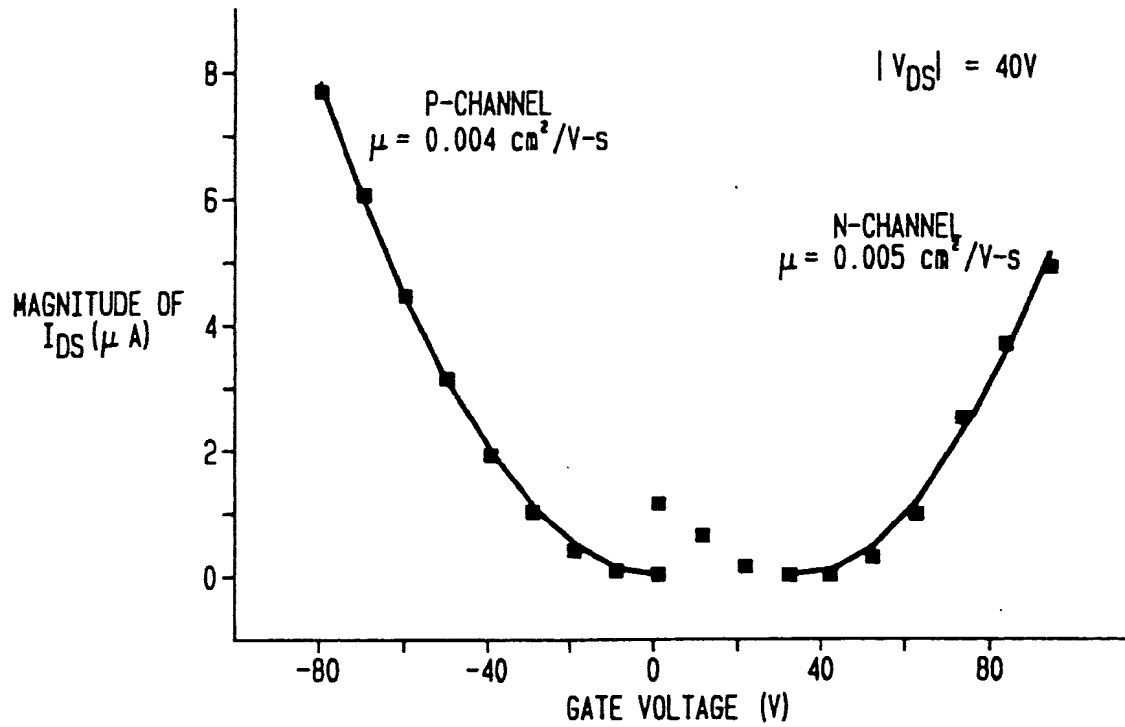
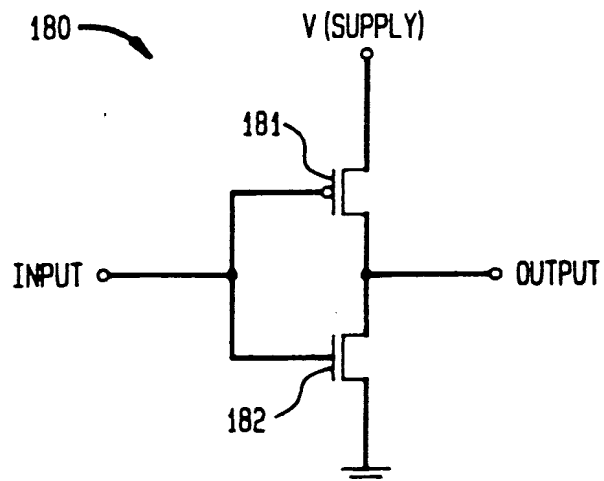


FIG. 18



## Description

### Field of the Invention

This invention relates to an organic thin film transistor (TFT) and more specifically to TFTs with enhanced carrier mobility.

### Background of the Invention

Organic TFTs are generally composed of in sequence a conductive gate electrode, a layer of gate insulator, a thin (less than 1 micron in thickness) layer of active (semiconductive) organic material and two laterally-spaced conductive strips as source and drain electrodes. The transistor can operate either in the enhancement or in the depletion mode depending on the polarity of the voltage applied to the gate electrode.

The first examples of organic TFTs were based on two organic conjugated polymers, polyacetylene (for example, F. Ebisawa et. al. J. Appl. Phys. 54, 3255 (1983)) and polythiophene (for example, A. Assadi et. al. Appl. Phys. Lett. 53, 195 (1988)). Organic TFTs have also been fabricated with organic molecular semiconductors, such as metallophthalocyanines (for example, G. Guillaud et. al. Chem. Phys. Lett. 167, 503 (1990)) and  $\alpha$ -sexithienyl (for example, X. Peng et. al. Appl. Phys. Lett. 57, 2013 (1990)).

In addition to low cost, abundance of raw materials, and the possibility of large-area applications by using the simple techniques of spin coating and vacuum evaporation, organic TFTs have the advantage of low process temperature, typically less than 200 °C, as compared to conventional polycrystalline or amorphous silicon based thin film transistors, which generally require a process temperature above 350 °C. The low process temperature allows organic TFTs to be fabricated on plastic substrates, which are generally vulnerable to high temperature. Organic TFTs on plastic substrates are attractive for portable, thin, light-weight, flexible active-matrix display applications such as plastic liquid crystal displays, plastic organic and inorganic electroluminescence displays.

Up to now, the development of organic TFTs has been hindered by the poor semiconducting properties of the organic materials used, exemplified by their carrier mobility value  $\mu$  as low as  $10^{-4}$  to  $10^{-5}$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>. One of the best organic TFTs is based on  $\alpha$ -sexithienyl reported by Garnier and co-worker with carrier mobility of  $4.6 \times 10^{-1}$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> by manipulation of the gate insulator (Adv. Mater. 2, 592 (1990)). The result is comparable to those of hydrogenated amorphous silicon in a conventional MISFET, but the device is far from practical due to the hygroscopic property of the gate insulator used.

It is a purpose of this invention to disclose a new organic TFT structure that provides an organic TFT with enhanced carrier mobility.

It is another purpose of this invention to provide an

organic TFT on plastic substrate for flexible, light-weight, large-area, display applications.

### Summary of the Invention

The above described problems and others are substantially solved and the above purposes and others are realized in an organic thin film transistor including a gate electrode, a layer of gate insulator material, a source electrode, a drain electrode and a layer of uniaxially aligned organic semiconductor material positioned between or underneath the source and drain electrodes, wherein the alignment of the organic semiconductor is achieved by a layer of an orientation film positioned adjacent the organic semiconductor.

In the above organic TFTs, the alignment of organic semiconductor material between the source and the drain electrodes by the means of the orientation film enhances the carrier mobility from the source to the drain as compared to the un-aligned (random oriented) organic semiconductor.

### Brief Description of the Drawings

Referring to the drawings, wherein device feature dimensions are often in submicrometer ranges, so that the drawings are scaled for ease of visualization rather than dimensional accuracy:

FIG. 1 is a cross section view of a conventional organic TFT structure; and  
FIGS. 2,3,4,5,6 and 7 are cross sectional views of six variations of an organic TFT structure in accordance with the present invention.

### Description of the Preferred Embodiments

The present invention is directed to an organic thin film transistor with an orientation film underneath the organic semiconductor for the purpose of aligning the organic semiconductor material to enhance the carrier mobility between the source and the drain electrodes.

As is illustrated in FIG. 1 a typical traditional organic TFT 10 includes a gate electrode 11 made of a stable metal, a metal alloy, or a transparent conductor such as indium-tin-oxide, a gate insulator 12 composed of a dielectric medium such as SiO<sub>x</sub>, SiN<sub>x</sub>, AlO<sub>x</sub> or organic polymeric dielectric medium, an organic semiconductor film 13 selected from either an organic polymeric semiconductor material or an organic molecular semiconductor material, and two laterally spaced conductive strips 14 and 15 made of a stable metal, a metal alloy, or a transparent conductor such as indium-tin-oxide, as a source and a drain electrode.

In the prior art, organic TFTs (e.g. TFT 10) generally suffer from poor device performance as compared to conventional polycrystalline, amorphous silicon transistors, mainly because of the very low carrier mobility